MECHANICAL IMPROVEMENT OF HARDENING AND TEMPERING STEEL WITH THE ADDITION OF SiC AND TiCN NANOPARTICLES IN THE STEEL MELT

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ABSTRACT:

Novel processing technologies have allowed the reinforcement of several steel grades and alloys through the fine dispersion of different types of particles. However, the addition of ceramic particles in the steel melt causes agglomeration and coarsening phenomena. For this reason, little research has been carried out to add ceramic particles in steel in the traditional steelmaking process.

Here we report a hardened and tempered steel grade that is reinforced for the first time through the addition of ceramic nanoparticles, such as TiCN and SiC, into the steel melt at laboratory scale. The results obtained from the tensile tests and hardness measurements reveal the mechanical behaviour of the steel grade is enhanced after the addition of the nanoparticles.

Keywords: Hardened and tempered steel; Nanoparticle; Laboratory scale casting; Microstructure; Grain refinement; Solid solution hardening; Mechanical properties

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1.- INTRODUCTION

The reduction of CO_2 emissions, closely linked to weight and energy consumption, is essential to tackle climate change. For this reason, different industrial sectors, such as the steel and transport sectors, focus on product and process efficiency. In this context, the manufacture of lighter components has become one of the main goals pursued by steelmakers during the last decades.

One of the strategies followed to manufacture lighter steel components is the steel mechanical enhancement [1]. Other alternatives are the incipient investigations on low density steels, or the traditional redesign of steel components. Mechanical enhancement of steel can be obtained through different microstructural mechanisms such as grain refinement, solid solution strengthening, precipitation strengthening, and work hardening [2]. In this context, the design and development of novel steel grades through innovative compositions and processes are essential. Hardened and tempered steels are good candidates for tailoring mechanical properties, as they are produced with compositions and thermal treatments that can be modified in different ways to provide the steel with a wide range of properties.

In addition, these steel grades represent outstanding materials to manufacture a variety of components for the tool and transport sectors [3-4].

The addition of nanoparticles constitutes an innovative strategy to enhance the mechanical properties of the steel matrix, for example reinforcing the microstructure through the grain refinement, which could increase the mechanical strength of the steel without detrimental effects on the elongation. Several studies report the beneficial effect of non metallic inclusions on the microstructure and mechanical properties of steel [5-6]. In particular, the mechanical behaviour of two phased systems formed by steel matrix and inoculants can be monitored through the fine control exerted by nanosized dispersoids on the steel microstructure [7-13]. Although the fabrication of metal matrix composites [14-18] has been also attempted through the traditional steelmaking process, recent processing technologies developed in the last decades [19-22] have allowed a more controlled manufacturing process. However, these technologies involve higher production costs and sophisticated equipment.

Here we report the reinforcement of a hardened and tempered steel grade through the addition of ceramic nanoparticles in the steel melt at laboratory scale.

2.- MATERIALS AND METHODS

The steel grade used in this investigation, and here referred to as 20MnCr, is a steel grade used in the automotive sector for the fabrication of nuts, tripods, and gears, and has the following composition (wt.%): C (0.20), Mn (1.20), Si (0.10), Cr (1.14), Ni (0.14). Commercial nanopowder of Silicon carbide (SiC) and Titanium carbonitride (TiCN) was used to feed the steel bath: *Neomat Co.* SiC (average particle size = 50±5 nm, 99.93% purity); *Neomat Co.* TiCN (average particle size = 40±5 nm, 99.90% purity). Nanoparticles were safely handled in a lamellar air flow cabinet. They were packed in Aluminium foil before being added into the steel melt. The steel was melted in a levitation induction furnace under protective atmosphere and rapidly cast in a water cooled Copper mold. The samples were forged and thermally treated using a Nabertherm muffle type furnace. The chemical composition of the treated samples was analysed by means of LECO® CS-400 Carbon/Sulfur Determinator, Optical emission spectrometry (Varian Vista-MPX simultaneous Induced Coupled Plasma – Optical Emission Spectrometry analyser), and Thermal conductivity (for Nitrogen content determination).

The composition and microstructure of the alloys were analysed by optical microscopy (LEICA microscope) and Environmental Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (ESEM-EDX). The microstructure of the samples was revealed with Nital etching and Picric acid etching. Using image analysis on acquired optical micrographs, Prior Austenite Grain Size (PAGS) was measured as the mean value of the equivalent circle diameters. The mechanical properties of the alloys at room temperature were measured using tensile test equipment (INSTRON 5501) and a FV-700 FUTURETECH Vickers Hardness Tester (10 Kg load).

3.- RESULTS

3.1.- EXPERIMENTAL PROCEDURE

Three steel grades were produced at laboratory scale (700 g) from the 20MnCr commercial steel grade: (a) 20MnCr (for comparison); (b) 20MnCr + nanoSiC; (c) 20MnCr + nanoTiCN. The fabrication process consisted in melting and casting the commercial steel grade 20MnCr, with the addition of 0.5 wt% of SiC or TiCN nanoparticles packed in Aluminium foil into the steel melt, in the cases (b) and (c), respectively. The laboratory scale ingots produced (cylinders of 120 mm in length and 30 mm in diameter) can be observed in Fig. (1).

Fig. (1). *Levitation induction furnace (left); aspect of the laboratory scale as-cast samples (right)*

The three as-cast samples produced were forged at 850ºC and thermally treated (austenitization at 940ºC, quenching, and tempering) in an attempt to simulate at lab scale the industrial processing commonly applied to this type of steel grades (forging at 850ºC, carburising at 940ºC, quenching, and tempering). The forging reduction ratio applied was 2:1.

3.2.- CHEMICAL ANALYSIS

Table 1 shows the chemical composition of the three steel grades cast at laboratory scale.

Element	(a)	(b)	(c)
C	0.21	0.25	0.18
Si	0.12	0.23	0.11
Mn	1.25	1.13	1.22
Cr	1.19	1.19	1.22
Ni	0.096	0.05	0.096
Al	0.30	0.53	0.35
Ti	<0.010	<0.010	<0.010
N	0.0096	0.0059	0.0144

Table 1. *Composition (wt%) of the three as-cast steel samples (a), (b), (c)*

As it can be seen in Table 1, the C and Si contents are increased in (b) as a result of the SiC nanoparticle addition. The Al content is high in the three as-cast samples due to the addition method, and considering that, in (a), an amount of Al similar to that incorporated to (b) and (c) was added for comparison. The presence of TiCN in (c) can be only revealed through the high N content detected with respect to (a) and (b).

3.3.- CHARACTERIZATION

After forging and treating, the three steel grades were characterized in terms of microstructural and mechanical properties.

The microstructure of the samples was analysed by optical microscopy after etching with Nital and Picric acid, in order to reveal the tempered martensite microstructure formed at the end of the hardening and tempering treatment, and the prior austenite grain structure formed in the austenitization process, respectively (Fig. (2-3)).

Fig. (2). *Microstructure of the three steel samples (above from left to right: (a), (b), below: (c)) after treatment (Nital etching)*

The martensite after tempering can be observed. The microstructures of (a) and (b) appear more homogeneous than that observed for (c) (Fig. (2)).

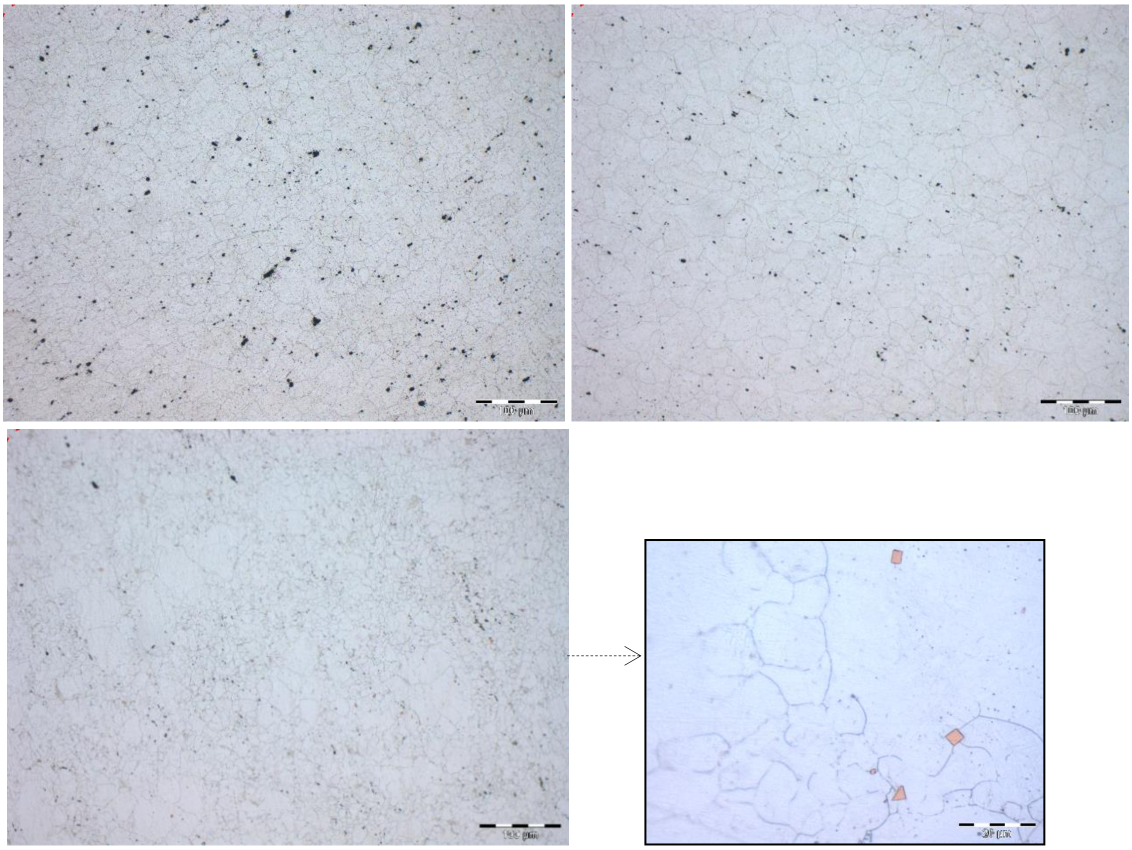

Fig. (3). *Microstructure of the three steel samples (above from left to right: (a), (b), below: (c) including a magnification of TiN precipitates on the right) after treatment (Picric acid etching)*

The prior austenite grain structure formed in the austenitization process can be observed with slight differences in the Prior Austenite Grain Size (PAGS). The microstructures of (a) and (b) appear more homogeneous than that observed for (c) (Fig. (3)).

In Fig. (3), it can be observed that the average PAGS of (a) and (b) is 20-25 µm, whereas, in the case of (c), two different PAGS are present: 12 µm and 50 µm. The smaller PAG of (c) exhibits orange polygonal precipitates in the grain boundaries that could correspond to TiN precipitates of approximately 4 µm of equivalent diameter.

In order to clarify the composition of the precipitates observed in (c) and study the microstructure of (a) and (b) in more detail, an ESEM-EDX analysis was performed on the samples etched with picric acid. As shown in Fig. (4), the microstructure of the samples observed by optical microscopy is confirmed. The prior austenite grain structure formed in the austenitization process, together with the inclusions and precipitates formed after treatment, can be observed.

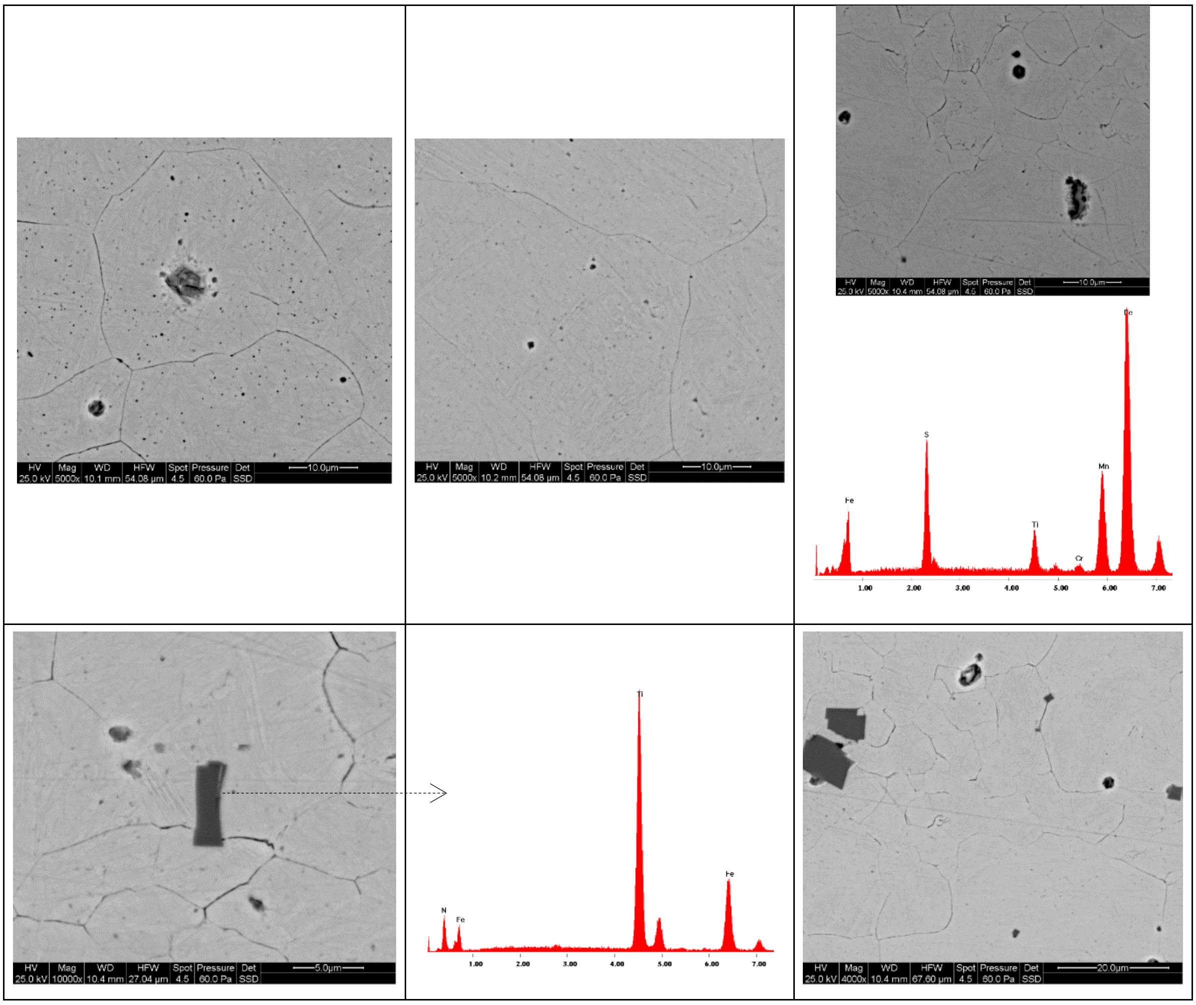

Fig. (4). *Microstructure of the three steel samples (above from left to right: (a), (b), (c); below: (c)) after treatment (Picric acid etching)*

As it is observed in Fig. (4), in (a) and (b) samples, MnS inclusions can be observed, as well as Aluminium oxides, distributed in a matrix rich in Al and Si. In the case of (c), also MnS inclusions are observed. However, for this sample, the PAG is much more heterogeneous than for the rest of samples, with dark inclusions containing Mn, S, and Ti, and polygonal precipitates containing Ti and N and located in the PAG boundaries. TiCN nanoparticles could have reacted in the steel melt, giving rise to secondary precipitates of the above mentioned compositions. As it happens in (c), TiN precipitates found in steel usually appear as rectangular inclusions of micrometer size [23-24].

The Vickers hardness (10 Kg load) and tensile properties of the three steel samples were measured for comparison (Tables 2-3).

Steel Sample	(a)	(b)	(c)
HV10	466±7	496±4	463±8

Table 2. *Average values of Vickers hardness (10 Kg load) for the three steel samples*

As it can be seen from Table 2, the hardness of (b) is considerably higher than that offered by samples (a) and (c).

In Table 3, the tensile properties of the three steel grades are shown. As observed, the samples with nanoparticle addition, (b) and (c), exhibit mechanical properties improved with respect to the reference sample (a). According to the tensile and hardness results, the mechanical enhancement is especially noticeable with the addition of SiC nanoparticles.

Steel Sample	(a)	(b)	(c)
Tensile Strength (MPa)	1450	1536	1425
Yield Strength (MPa)	1143	1206	1160
Elongation (%)	10.7	12.5	14
Reduction of Area (%)	44.2	50	50

Table 3. *Tensile properties of the three steel samples*

4.- DISCUSSION

The mechanical properties observed for the three steel samples are in good agreement with their respective microstructures. In (c), the pinning effect of TiN precipitates, formed from the TiCN nanoparticles added, on PAG boundaries can contribute to grain refinement, thus increasing mechanical strength and ductility of the steel sample. However, the presence of dual PAGS in (c), which could be the evidence of a partial grain refinement as a result of TiN in some parts of the microstructure, could be detrimental to the mechanical behaviour and consequently reduce the strength increase in this material to some extent. In the case of (b), the increase observed in terms of hardness and tensile properties is in good agreement with the increase experimented by similar cases reported in the literature, where SiC nanopowder is added [25]. Nevertheless, as the steel melting implies the dissolution of SiC, no SiC nanoparticles or derived precipitates have been detected in the microstructure, so the strengthening effect observed in this case can be attributed to solid solution hardening.

The experimental research here reported explores the different strengthening mechanisms to which the addition of nanoparticles can contribute for the mechanical improvement of hardening and tempering steels. Future investigations will be necessary to explore how to successfully scale up the addition of nanoparticles at industrial level and the effect of inoculated nanoparticles at such scale, as some research carried out in this context supports the possibility of steel mechanical enhancement at experimental scale but faces several drawback at industrial scale related to coarsening phenomena and low addition yields [26].

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